DIOXIN SAMPLING AND ANALYSIS OF SELECT MUNICIPAL DRINKING WATER SOURCES IN THE ATHABASCA AND PEACE RIVER BASINS

Alberta
ENVIRONMENT

DIOXIN SAMPLING AND ANALYSIS OF SELECT MUNICIPAL DRINKING WATER SOURCES IN THE ATHABASCA AND PEACE RIVER BASINS

JULY, 1990

ALBERTA ENVIRONMENT

ENVIRONMENTAL PROTECTION SERVICES

90-06684/

SUMMARY:

Public awareness and concern regarding the presence of chlorinated dioxins and furans in bleached kraft mill effluent resulted in a concern as to the impact of such wastewater discharges on drinking water supplies. This concern was raised by a number of Alberta municipalities downstream of existing and planned bleached kraft mill developments. Therefore, a dioxin/furan sampling program was undertaken at select communities downstream of existing pulp mills to address this issue. The purpose of the program was to determine the levels of dioxins/furans in both raw and treated drinking water, and with this information assess whether drinking water quality had been impacted unduly. The resultant data set would serve as a baseline for possible future comparisons of river quality.

Seven municipalities were identified for sampling and 14 sample sets (raw and treated water) were collected and subsequently analyzed for various chlorinated dioxins and furans. A sample set consisted of four 11 litre samples of water: duplicate samples, a field spike sample, and a field blank.

A number of sampling and analytical quality controls were incorporated into the study to assist in screening the raw data generated by the sampling program. These controls were essential given the fact that extremely low detection levels were sought (at the parts per quadrillion level). At such low levels interferences or minute contamination could arise easily from internal or external sources leading to spurious results.

A sample acceptance protocol was also established in advance of the study to assist in achieving a consistent and unbiased interpretation of the raw analytical data. The prime acceptance criteria were: for an analytical result to be accepted as valid, the sample must have met the study quality control and assurance criteria; for a result to be accepted as positive, the data must not only have been judged valid but also have a value above the method detection level (MDL) for the

particular chlorinated dioxin/furan congener group. The following additional acceptance criteria also were applied to determine whether a measured level of chlorinated dioxin/furan should be considered a positive value:

1) the field blank for the specific sample set was negative (i.e., no apparent field contamination);
2) a positive result appeared in both of the duplicate samples (i.e., sample collection was both representative and consistent);
3) field spike recoveries were reasonable -- generally within the 70%-130 % recovery range (i.e., the sample matrix did not result in undue interferences, and secondly, that the laboratories achieved acceptable levels of accuracy and precision); and
4) a positive result on a treated sample was accompanied by a positive result in the corresponding raw water sample. (This final criterion was applied with caution as the converse statement might not be true. The implication is that the raw water would be the source of dioxin and thus the criterion provided a further measure of the internal and external consistency of the data. There is little previous evidence to suggest that chlorinated dioxins/furans are produced under drinking water chlorination conditions in comparison to the very harsh chlorination conditions employed in bleached kraft mills.)

The concept of a methods detection level was utilized in this study. This involved a calculation of levels based on analyses of samples with varying matrix conditions and quantities of dioxin material. The method detection levels for the several dioxin components were determined from the results of field spike samples. A method detection range of 6-70 parts per quadrillion (ppq) was achieved. The less chlorinated dioxins or furans (e.g. tetra-, penta- and hexa-isomers) had method detection levels at the lower end of the range -- generally about 6-30 ppq -- while the method detection level for the octa-dioxins or furans approached 70 ppq.

Using the above criteria, no chlorinated dioxins/furans were detected in either the raw or treated drinking water samples collected during this sampling program. As the sampling was done during what was considered to

represent worst case conditions (i.e., minimum river flows) the implication is that within the limitations of the sampling methodology, there does not appear to be contamination of downstream drinking water supplies occurring from chlorinated dioxins/furans from existing bleached kraft pulp mill discharges at this time. Moreover, a valuable baseline for chlorinated dioxin/furan information was established for the Athabasca and Peace watersheds, which will permit future comparisons with new mill developments.

Lastly, from the quality assurance and controls in place for the study there was an indication that possible trace contamination of some samples may have occurred in this study. The origin of the contamination could not be identified. The extensive control measures, while unable to fully prevent spurious results, proved invaluable and necessary in the interpretation of the raw data and thereby prevented an inappropriate assessment. Improvements in sampling and laboratory procedures would be necessary for any future dioxin work.

TABLE OF CONTENTS

SUMMARY 1
Table of Contents 4
List of Tables 5
List of Figures 6
1. Introduction 7
2. Study Design 13
   a) Analytical Services 13
   b) Selection of Sites 14
   c) Sampling Protocol 15
   d) Seasonal Concerns 17
   e) Detection Limit Considerations 18
   f) Assessment Criteria 19
3. Quality Assurance/Quality Control 23
   a) Laboratory Validation 23
   b) Field Sampling Controls 24
   c) Laboratory QA/QC Measures 25
4. Analytical Results 27
5. Discussion and Conclusions 40
   References 42
   Appendices 43
   Appendix A -- Normalized Data
   Appendix B -- Raw Data (in three separate reports as an attachment to this report)

List of Tables

Table 1 Dioxin/Furan Congener Toxicity Comparison 11

Table 2 Field Blank Analyses 29

Table 3 Field Spike Design Dosage Levels 31

Table 4 Average Low Level Spike Recoveries 32

Table 5 Average Intermediate Level Spike Recoveries ...33

Table 6 High Level Spike Recoveries 34

Table 7 Calculated Methods Detection Limits and Instrument Detection Limits 37

Table 8 Summary of Dioxin Sampling Results 38

List of Figures

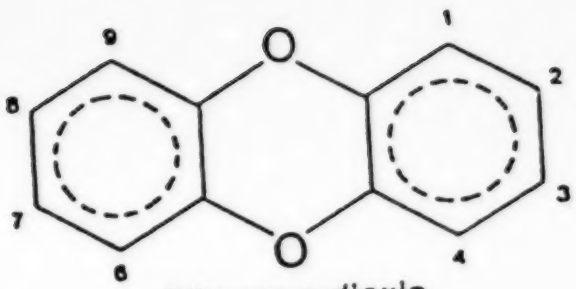
Figure 1 Dioxin/Furan Basic Structures Showing Chlorine Substitution Positions and Numbers of Isomers 8

1. Introduction

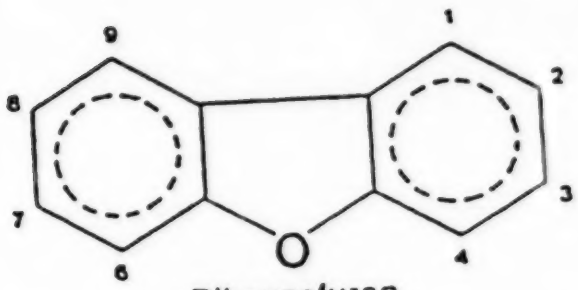
Recent proposals for additional forest industry development within Alberta raised concerns in a number of communities as to the possible contamination of their water supplies with "dioxins". The concerns stemmed from the fact that some members of the dioxin family of compounds have received wide spread media attention as being toxic, and in recent years these compounds have been detected as unintended by-products in effluents from conventional bleached kraft pulp and paper mills.

The chlorinated dioxins and furans are more appropriately known as chlorodibenzo-p-dioxins, consisting of 75 possible isomers depending upon the degree of chlorine substitution of the basic dioxin structure, and the chlorodibenzofurans, consisting of 135 possible isomers. The chemical structure and possible chlorine substitution pattern for the various chlorinated dioxin/furan isomers is depicted in Figure 1. Given that there may be up to a total of 210 isomers, it is generally more convenient to refer to smaller groups of isomers with the same degree of substitution, referred to as congeners, with the more common congeners being the tetra to octa congeners (four to eight chlorine substitution).

For the purposes of this report, the 210 chlorinated dioxin/furan isomers will be referred to collectively simply as dioxins. Where there is a need to be more specific then reference will be made to the individual congener group or appropriate compound.



Dibenzo-p-dioxin



Dibenzofuran

Number of Chlorine Substituents	Number of CDDs	Isomers CDFs
1	2	4
2	10	16
3	14	28
4	22	38
5	14	28
6	10	16
7	2	4
8	1	1
total	75	135

Figure 1

Dioxin/Furan Basic Structures Showing Chlorine Substitution: Positions and Numbers of Isomers

From: Clement and Tosine, Mass Spectrometry Reviews 1988, 7, 594

Dioxins have been detected in various matrices such as surface waters, sediments, food, select paper materials, and in a variety of other residues (2). The added attention and focus on the dioxins has resulted in significant improvements in sampling and analytical methods with various claims for very low detection limits. There is now a perception that low levels of dioxins may be rather commonplace in the environment.

Dioxins/furans were first identified as by-products of a number of chemical manufacturing processes. It has now been shown that these compounds can be produced in a variety of ways (primarily associated with incomplete combustion of chlorine containing materials), including the waste incineration of chlorinated materials and through forest fires. The resultant dioxins are present generally as particulate matter. It appears that once present in the environment, these chemicals are relatively persistent especially when protected from ultraviolet radiation through binding to other particulate material. Dioxins may also bioaccumulate implying an increased potential hazard.

Dioxins have been shown to exhibit very potent toxicity in select test animals. The public attention has come about from the attempted extrapolation of the animal toxicity data to possible human exposure. The dosage needed to cause toxicity appears to vary widely, depending upon the test animal studied as well as the degree of chlorine substitution; effective toxic dosages have been shown to range from 1 to 5000 ug/kg body weight of the test organism. The most toxic component of the dioxins has been identified as 2,3,7,8-tetrachloro-dibenzo-p-dioxin (2,3,7,8-TCDD); other dioxins and furans have been rated from 2 to 1000 times less toxic than 2,3,7,8-TCDD (see Table 1).

There is some debate in the literature as to whether the chlorinated dioxin animal toxicity data bears any relationship to human health; however this point has been lost in the ensuing public debate on environmental toxicants in general(1). For example, in those few cases where actual human accidental exposure to dioxin material has occurred, no deaths have been attributable to the exposure, while the resultant

human health effects (chloracne and general ill-feeling) have been reversible. Despite this information the image of dioxins as potent human toxicants persists.

Table 1

Congener Toxicity Comparison

(Relative to 2,3,7,8-TCDD)

Congener Group	Toxicity Relative to 2,3,7,8-TCDD
Dioxins	
Monochlorodioxins	0.0001
Dichlorodioxins	0.001
Trichlorodioxins	0.01
Tetrachlorodioxins (excluding 2,3,7,8-TCDD)	0.01
Pentachlorodioxins	0.5
Hexachlorodioxins	0.1
Heptachlorodioxins	0.01
Octachlorodioxins	0.001
Furans	
Monochlorofurans	0.0001
Dichlorofurans	0.0001
Trichlorofurans	0.01
Tetrachlorofurans	0.1
Pentachlorofurans	0.5
Hexachlorofurans	0.1
Heptachlorofurans	0.1
Octachlorofurans	0.001

Source: DIOXINS AND FURANS: THE CANADIAN PERSPECTIVE by the Canadian Council of Resource and Environmental Ministers and unpublished reports

Human exposure to the dioxins/furans may occur in many ways, but the pathways of most concern appear to be the ingestion of contaminated food or the inhalation of airborne contaminants in the vicinity of large combustion sources. Conversely, pathways involving exposure to "soil or drinking water are not considered as important in light of the relative concentrations normally involved "(3).

The Ontario Ministry of the Environment has proposed an interim standard for dioxins in drinking water. A value of 15 parts per quadrillion on a 2,3,7,8-TCDD equivalent basis has been suggested. Equivalency is determined by using toxicity factors similar to those listed in Table 1 to convert observed concentrations of detected congener groups to an equivalent 2,3,7,8-TCDD value. It is evident from Table 1 that should the mono- to tri- and the hepta- and octa- congener groups be detected their relative contribution to an equivalent value would be proportionately small.

2. Study Design:

The overall objective of this monitoring program was to establish whether dioxins are present in the drinking water obtained downstream of wastewaters discharged from existing bleached kraft pulp and paper mills. The information collected would assist in addressing the "safety" of these drinking waters and serve as a baseline for comparison to possible changes in dioxin levels with future developments.

a) Analytical Services

A major factor in the design of the monitoring program was the question of analytical services. Few laboratories in Canada or the United States have the demonstrated capability of performing dioxin analyses. At the time of this study, no laboratory in Alberta was performing routine dioxin analyses. Initially, consideration was given to the use of Wellington Environmental Consultants Incorporated of Guelph, Ontario for analytical services. However it became apparent that given the magnitude of the work, including the possibility of necessary follow up monitoring, it would be desireable to encourage the development of appropriate analytical capabilities locally; of course with the provision that the immediate program would not be compromised.

It was considered that a local laboratory could at a minimum perform some of the necessary pre-analytical preparatory services (bottle preparations, spiking solutions, blank water, etc.) as well as the preliminary processing of the samples (extraction and cleanup) which would eliminate the need to send large volumes of liquid samples to Ontario; this was an important factor given that sampling was being done in mid-winter. Furthermore, such an arrangement would simplify program logistics overall as only a very small extract volume need be shipped to Ontario for the final step in the analysis.

Enviro-Test Laboratories in Edmonton previously acted as a subcontractor to Wellington Environmental Consultants Inc in facilitating dioxin analysis work from Alberta. Based on this past experience, Envriro-Test made a proposal to co-ordinate the laboratory aspects of

this study, primarily for the opportunity to participate directly in the dioxin monitoring program and thereby achieve technology transfer benefits to both parties at no additional cost/risk to the study. Enviro-Test's proposal was accepted and resulted in the firm acting as the prime contractor for analytical services, with responsibility for providing the necessary support services, sample extraction, extraction clean up, and preparation of a final extract for analysis by Wellington. Furthermore, Enviro-Test offered to undertake complementary analysis of the final extracts at its own cost, thereby providing an additional level of quality control to the study not originally envisaged.

b) Site Selection

Presently all existing and proposed bleached kraft mills in Alberta are located in the Athabasca and Peace river basins. Only a limited number of communities actually withdraw water downstream of these existing mills. For the purposes of the monitoring program, four community sites were identified for sampling on the Athabasca and three on the Peace. The individual community identity was coded for the purpose of the laboratory analysis and within this report for ease of data presentation.

The following is the coding system that was used:

Athabasca River:

Communities: E-Jasper-river water only -- as a control site; D-Hinton; B-Smith; and A-Athabasca

Peace River:

Communities: F-Grande Prairie-as a control site; G-Peace River; and C-Fort Vermilion

Both raw and treated water samples were taken at each municipality, the exceptions being site E-Jasper where only direct river water sampling was done (as a control on the river), and at site D-Hinton where an additional intermediate sample was taken (an intermediate pumping facility exists at the site). In total, fourteen sample sets at seven

municipal locations were obtained. Collection of both raw and treated water samples was desired to address the issue of production or removal of dioxins by the water treatment processes. Questions on this issue were expected if only treated water samples were to be collected.

c) Sampling Protocol

In general, the sampling protocol used for this study followed the procedure developed by the Ontario Ministry of the Environment. More specifics are provided below.

A sample set at a site consisted of four subsamples of approximately 11 litres each (3 four-litre bottles per subsample). A sample set consisted of:

a field blank;
a field spike;
a regular sample; and
a duplicate regular sample.

Field blanks were obtained by taking 12 litres of HPLC grade distilled water to the site and filling the designated blank bottles in approximately the same fashion as the regular samples.

Field spike samples were obtained by dosing one or more of the designated spike bottles with a laboratory prepared ampoule of a dioxin/furan "cocktail". All of the spike ampoules were made from the same dioxin/furan mixture; a low level spiking concentration was achieved by adding a spike ampoule to only one of the three sample bottles that constituted the spike sample; an intermediate or high spike level was achieved by adding a further spike ampoule to the second or third bottle as necessary.

The spike sample, which would have been obvious due to the presence of an ampoule in the bottle(s), was disguised from the remainder of the sample set by adopting the policy of adding a methanol-containing ampoule to all of the remaining bottles in the sample set.

Sampling was carried out by a two-man team. The same team undertook the sampling at each of the selected municipal sites. Sampling spanned the weeks of February 6, 1989 to February 27, 1989.

The basic sampling protocol used is outlined below:

a) Once the specific sampling location at the water treatment plant site was selected, the water tap/source was allowed to run for at least 15 minutes to clear lines and ensure fresh water was being sampled.

b) All sample bottles were labelled with their tops still on and arranged for the actual sampling.

c) The tops from all bottles were removed and placed face up on paper towelling. Each bottle was then filled with sample or blank water as the case may be to the 1/4 mark in the following sequence: regular samples bottles 1-3, duplicate sample bottles 1-3, spike bottles 1-3 and lastly the blank bottles. The blank bottles were 1/4 filled with HPLC grade distilled water from separate containers (sealed after each pouring). The filling sequence for all bottles was repeated three times in succession to obtain the desired volume within a timeframe of approximately 45 minutes.

d) All tops were then replaced on the bottles. Based on the number of dioxin/furan ampoules that were to be added to the spike sample, i.e., either one, two or three spikes ampoules, methanol blank ampoules were first added to all the other samples. The ampoules were added by removing each sample bottle cap in turn, breaking the ampoule just above the bottle and allowing the entire ampoule and its contents to fall directly into the sample bottle. The bottle cap was then immediately replaced. Once the methanol blank ampoule addition had been completed, the spike ampoules were added in a similar fashion to the remaining identified spike sample bottles.

e) The bottle exteriors were dried using paper towels and the bottles than placed in cardboard shipping containers for transport back to the analyzing laboratory. Since the samples were being shipped in mid-winter, care was taken to prevent freezing and to ensure that all samples from a location reached the laboratory within 24 hours of collection.

Special Notes:

i. No samples were taken at a location where smoking was occurring although atmospheric smoke was present and prevalent at one site during sampling. (The teepee burner of a nearby saw mill was in operation during the day the sampling was conducted at site B. Inversion conditions at the time resulted in the smoke from the burner enveloping the treatment plant site.)

ii. New latex gloves were used by the sampling crew during each sampling event and discarded when the sampling was completed at the site.

iii. All samples with the exception of those from location C were transported back to the analyzing laboratory in Edmonton by the returning sampling team. The samples from location C were shipped by a commercial carrier as a means of protection against freezing.

iv. The samples at location E were not composited quarterly as described in item 4 of the above procedure; instead each bottle was filled completely in succession and directly from the source by immersion of the sample bottles. With this exception, all of the remaining sampling procedures at site E were the same as for the other sites.

d) Seasonal Concerns

It was recognized that variations in the levels of dioxins within a river basin may occur depending upon seasonal flow patterns. It was

assumed that the emission of any dioxin material from mill sources should be relatively constant. Since low flows in a river generally occur under winter ice conditions, the worst case scenario (ie., highest expected potential dioxin concentrations) was assumed to be the winter. The sampling was therefore organized accordingly and done in February, 1989.

e) Detection Limit Considerations:

Practical levels of detection are dependent upon a number of factors including the matrix that is being sampled, the instrumentation being used for the analysis and the skill of the analyst. Dioxin analysis is commonly done using any one of several variations of gas chromotography/ mass spectroscopy (GC/MS) methodology. The initial analytical step involves sample extraction whereby any dioxins present are extracted from the sample matrix (in this case raw or treated drinking water), followed by a clean up procedure to eliminate unwanted and interfering organics that may be extracted along with the dioxins. The final step involves the analysis of the cleaned extract on the particular GC/MS system, screening specifically for dioxins. For this study Enviro-Test utilized a portion of each extract for its analysis, and the remaining portions of the extracts were shipped to Hellington for re-analysis.

For liquid matrices it is generally accepted that detection levels in the low parts per trillion or even lower ie., in the parts per quadrillion range, are possible. For this study a detection level at several parts per quadrillion was considered necessary in view of the very low standard for dioxins in drinking water being discussed at the national level. There was also the practical consideration that anticipated raw water concentrations would be at the same order of magnitude as the possible detection level given the large dilution available to mill effluents within the two river systems.

Based on a recent Environment Canada-sponsored laboratory round-robin, a practical lower level of 2-6 ppq could be expected from a liquid matrix when considering the lower congener groups. The higher

congeners such as the octa congeners, however, are more difficult to recover and detection levels for these compounds could range an order of magnitude greater or more. Both laboratories demonstrated their ability to achieve the desired range of detection before the study commenced.

There was a distinction made between an instrument detection level i.e., the determineable value at some arbitrary signal height above baseline noise level of the instrument for an individual sample, and the method detection level which represents the statistical determination of a non-zero value based on a number of samples with varying matrices. The method detection range was considered of more significance as it provides a means of accounting for the accumulation or variation of errors in the overall analytical methodology, not just the analytical sensitivity of the particular instrument. The method detection level concept was adopted for this study and thus necessitated the use of field spike samples at differing concentrations to assess directly overall laboratory performance and method performance. In addition, both laboratories were using low resolution GC/MS which made it somewhat more difficult to confidently report very low level potential hits (in comparison to high resolution work) giving further weight to the method detection concept.

To achieve a detection level in the 5 ppq range required a large sample volume, in the order of 8-12 litres per sample. In this study, 3 x four litre samples were collected to constitute one specific sample of an effective volume of 11 litres. In addition, field spike samples were collected at each of the 14 sampling sites, thereby providing a limited basis on which to calculate an actual method detection limit rather than relying solely on instrument detection/performance based on laboratory added surrogates.

f) Assessment Criteria

Extreme care and attention was used in establishing the criteria that determined whether or not dioxins were actually present in a sample. At the very low detection level that was desired for this study, it would be very easy to obtain either false negative data by having unacceptable

losses or noise, or false positive data from low level sample contamination. One obvious source of sample contamination would be ambient air particulate contamination: i.e., vehicle exhausts, fireplaces, wood waste burners, and possibly even contamination from cigarette smoke. Other sources of contamination or interference could occur during the processing and analysis steps within the laboratory.

While various quality control/assurance measures were taken to minimize both field and laboratory variations and possible contamination, it would still not be possible to categorically ensure all externally or internally generated contaminants would be prevented or eliminated. Therefore, the following additional assessment criteria were established at the onset of the study to assist in screening possible spurious results.

i) Analytical Data: Positive Field Blanks

Field blanks would be done at each sampling location to control for the actual sample collection protocol and subsequent processing. The presence of a positive field blank within the same order of magnitude as the regular sample would raise sufficient concern over protocol (site or laboratory) to qualify the validity of the regular sample of interest.

ii) Positive Regular Sample Data

For a regular sample to be positive several conditions would have to be met. Firstly, the sample set must have met the QA/QC criteria as being a valid sample set as per i) above. But in addition, the positive result must have appeared in both of the duplicate samples. Since it is expected that dioxins will be present on a continuous basis, taking duplicates provides a further measure of sample validity, and aids in detecting possible other field conditions that might affect the collection of a representative water sample. Given the large volume of liquid collected for each duplicate and that both samples would be collected at essentially the same time and

under the same conditions, should only one of the duplicate set be positive this would suggest that other factors are confounding the sample collection and/or analysis.

iii) Field Spike Recoveries

For a sample result to be considered a positive result the field spike recoveries would have to be reasonable. In the case of a relatively clean liquid matrix, recoveries close to the ideal of 100% should be attainable and attainable in a consistent manner. A more practical range would be 70-130% (as evidenced by earlier prestudy fortification in laboratory distilled water); as such the sample matrix is not resulting in undue interference or difficulties with regard to extraction. Field spikes help to control for both potential matrix problems as well as possible loss or degradation during collection and shipping, while surrogate spikes are also added at the laboratory at the start of extraction to establish procedural recovery efficiencies. Using a variety of spiking levels from the differing sampling sites allows for the calculation of a method detection range.

iv) Data on Sample Train

For a sample result to be considered a true positive, a positive result in a treated water set should be accompanied by a positive result from the corresponding raw water sample set. Dioxins have very low solubility in water (in the order of 20 parts per trillion --ppt), and thus it is expected that the dioxin will be in particulate form or readily and rapidly absorbed onto particulate material. Some of this particulate associated dioxin may pass through a treatment plant. Although water treatment processes have the ability to remove a significant portion of the particulate material commonly present in raw waters, in practice carry-over and filter breakthrough does occur, especially for fine, colloidal particulate. The expectation is that this particulate dioxin

material is the source of any dioxin that might be found in treated drinking water rather than the production of dioxins via chlorination within the water plant. On the other hand, the converse -- of expecting to find treated levels when raw water dioxins are detected at low levels -- may not hold because of the removal mechanisms noted above.

3. Quality Assurance/Quality Control (QA/QC)

A significant effort was made to incorporate as many QA/QC measures into the study as possible in view of the extremely low detection limits desired; the uncertainties that were still associated with the relatively new analytical testing procedure for dioxin; and the use of low resolution mass spectroscopy. Three major aspects of the QA/QC program are discussed below.

a) Laboratory Validation

There existed independent confirmation of the general capabilities for Wellington Environmental in performing dioxin analyses. No such confirmation existed for Enviro-Test Laboratories, the local Alberta company that had requested and subsequently was selected to act as the prime contractor for the study. Enviro-Test therefore agreed to undertake a small validation study at its own cost. The validation study involved the fortification of triplicate 12 litre samples of laboratory distilled water at three different spiking ranges -- 15 ppq, 30 ppq and 45 ppq of dioxins/furans -- and the subsequent determination of recoveries. The spiking values were chosen as being representative of the dioxin/furan levels expected to be encountered in the actual field survey. A total of nine spiked samples were thus obtained and analyzed using the analytical procedures that were to be employed in this study.The mean overall spike recoveries from the validation study varied from 60-90%, depending upon the specific congener group of dioxins and furans. The reported performance was within generally accepted limits that have been demonstrated through quality assurance/control work at the national level.

On the basis of this validation work, it was decided that Enviro-Test could adequately extract and clean up field samples for final analysis by Wellington. In addition, Enviro-Test offered to analyze all field samples, at their own cost, in parallel to the analyses by Wellington. This provided an added measure of confidence in the total database generated, as any significant discrepancies between laboratories would act as an immediate flag to possible analytical problems.

b) Field Sampling Controls

The best analytical procedures must be complemented by field sampling procedures that provide a fair and representative sample for analysis. Therefore, a number of measures were incorporated into the sampling protocol to control and ensure the quality of the samples being collected.

A well-defined sampling protocol was used in this study. The protocol was adapted from the procedures used by the Ontario Ministry of the Environment for their dioxin monitoring programs. Other routine precautions established were: i) using a set sampling team to ensure uniformity; ii) the manner of physically collecting and shipping samples and the keeping of field notes and other records; iii) reviewing for suitability all sampling materials that would be coming into contact with the source water; iv) obtaining specific grade and lot number of sample bottles to control against possible variation in glass quality and contamination during bottle production; v) obtaining the necessary quantities of HPLC grade distilled water to be used for the field blanks; and, vi) using metal or teflon tubing where necessary.

The principal field control measures consisted of the collection of a variety of additional samples at each site. Duplicate samples were collected at each site. This provided information on laboratory precision as well as an indication of variability of the analyze in the water source. It was anticipated that dioxins, if present, would be so on a continuous basis. Therefore a duplicate sample would also help to screen for possible spurious results.

A field spike sample was generated at each sampling site. The field spikes provided some measure of control for accuracy, precision and the recovery efficiency of the laboratory. The spike data would indicate whether there were specific matrix-related problems that affected the critical extraction step within the analytical protocol or if there was a deterioration of the sample between the time of collection and analysis. Ultimately, the field spike data was used to establish the practical method detection level for the study. The other major field control consisted of taking field blanks. This involved using the same sampling

protocol at each site but adding high grade laboratory distilled water, free of any contaminants, to separate sample bottles. The use of a blank provided further information on the quality of the analysis and possible other confounding factors or conditions in the field. The presence of contaminants in the blanks, regardless of whether of laboratory or field origin, would be very strong grounds for considering the data from the associated sample set as suspect. (It is recognized that additional laboratory blanks would have helped to distinquish between field or laboratory originated contamination; however, only two laboratory blanks were run during the study due to cost and lab restraints thereby making such a distinction impossible.)

c) Laboratory QA/QC Measures

The final area of QA/QC attention was adequate control within the analyzing laboratories.

Enviro-Test instituted a number of control measures to check for, and eliminate, cross-contamination while the samples were being processed. These measures included lockup of all dioxins/furans spikes and surrogates; separation of glassware for this study versus other routine work; separate work areas away from other parts of the laboratory; rigorous glassware cleanup; the use of new glassware for the study; undertaking several methods blanks (but cost and other constraints restricted being able to run a blank for every set of samples extracted); and, doing intermediate blanks during the extraction/cleanup process to make sure that sample material was not lost or that other chemical interferences were not present or introduced. (However, these intermediate screening checks were done at a much higher cut-off-limit for dioxins than the method detection range, principally to ensure that gross loss or interference was not occurring and thereby wasting the analysis effort.)

As part of the standard methodolgy for the analysis the laboratory added isotope-labelled spikes (known as surrogates) to each sample prior to extraction to control for extraction, cleanup and instrumentation problems. A further internal standard was added by both Enviro-Test and

Wellington to the reconstituted extract prior to analysis as an internal standard to control for instrument response and variations in analyst injection technique.

The laboratory QA/QC measures, coupled with the field controls were valuable in assessing the reliability of laboratory and sampling performance, and consequently assessing the significance of the data itself as to the presence/absence of dioxins.

4. Analytical Results

A considerable amount of raw data was generated during the course of this monitoring study. The raw data, which is provided in the several appendices to this report, is summarized for the purposes of a general presentation in this chapter.

a) Quality Assurance/Quality Control Data

As the desired detection range for this study was very low, in the order of several ppq, there were many possible opportunities to encounter interferences or high "noise" levels which might generate spurious results. The QA/QC data was reviewed first to determine whether or not the individual sample results constituted valid data.

The QA/QC data was also the means by which detection level claims could be verified and an appropriate methods detection level established.

1) Field Blanks

Field blanks were taken as part of the sample set for each site. In total, there were 14 separate field blanks. The results are presented in Table 2. Six of the 14 blanks (representing 5 of the 7 municipal locations in the study) showed varying amounts of contamination, predominately with low level furans. Of interest, but without explanation, is the apparent higher number of positive blanks at the treated sites relative to the raw sites.

The average concentrations of dioxins and furans, but predominantly furans, in those blanks showing trace values ranged from 3 ppq to a high of 49 ppq with an overall mean value for all six positive blanks of approximately 12 ppq. (Individual isomer values within a given blank sample ranged from 3 to about 70 ppq.)

An implication of these blank sample results is that low level contamination of some sort arose either in the field or at some point within the subsequent processing of the sample sets within the

laboratory. Regardless of the source of contamination, any actual result within the same order of magnitude as the positive blank for the same site is therefore considered suspect. A further implication is a regular sample would have to have dioxin levels greater than the blank mean (the blank mean plus 3 standard deviations) to be significantly above the "background noise" as represented by the blank data. However, as noted previously, it was not possible to do sufficient planned laboratory blanks to assist in detecting the cause of the contamination noted.)

(In reviewing the laboratory data, it appears that a set of samples, including the blank from Site B, which were processed together in the laboratory, all had approximately the same levels and distribution of observed furans/dioxin. This suggests the very low level contamination observed may have originated from within the laboratory as a discrete event. Nevertheless, without the laboratory blanks it remains a supposition only.)

Table 2

Field Blank Analyses

Location	Raw Site	Intermediate	Treated Site
A	nd	-	nd
B	xh	-	x
C	nd	-	x
D	nd	nd	nd
E	x	-	-
F	nd	-	x
G	nd	-	x

Notes: nd -- no dioxins/furans detected

x -- 1-12 ppq of furans detected with one or more congener groups present

xh -- levels up to 70 ppq of furans detected with a dioxin congener at low ppq levels also detected

ii) Field Spike Recoveries

A total of 14 blind field spike samples were submitted for analysis. Three different spiking doses of a standard dioxins/furans mixture were used. Seven of the samples were at the low dosage; four were at the intermediate dosage (2 times low dosage); and 3 were at the high dose level (3 times low dosage). Table 3 is a summary of the design spike concentrations for the three different dosage levels.

An overall average recovery for each spike sample was determined. The average spike recovery was taken as the mean of the individual recoveries for all congener groups in the sample. It is recognized that recoveries will vary with congener group and as such an average is not strictly correct; however, it does help to qualitatively compare the large data set. Using this approach, the average recoveries for the seven low level spikes are shown in Table 4. Table 5 is the summary for the intermediate level spike recoveries, and Table 6 is the summary for the high level spike recoveries.

Table 3

Field Spike Design Dosage Levels

(in ppq based on 11 litre samples)

Congener Group	Low	Intermediate	High
PCDD's (Polychlorinated dioxin group)			
TCDD (tetra)	18.2	36.4	54.6
PCDD (penta)	18.2	36.4	54.6
HCDD (hexa)	36.4	72.8	109.2
H7CDD(septa)	36.4	72.8	109.2
OCDD (octa)	54.6	109.2	163.6
PCDF'S (Polychlorinated furan group)			
TCDF	18.2	36.4	54.6
PCDF	18.2	36.4	54.6
HCDF	36.4	72.8	109.2
H7CDF	36.4	72.8	109.2
OCDF	54.6	109.2	163.6

Table 4

Average Low Level Spike Recoveries

(Per Cent Recoveries)

Sample Number	Wellington	Enviro-Test
1	45	71
34	109	128
60	72	100
55	100	159
45	93	117
22	66	127
30	88	127
Mean	82%	118%
Standard Deviation (SD)	22%	27%
% Relative SD (%RSD)	27%	23%

Two extremes of recovery are evident. Both laboratories had difficulties to a certain degree with quantitating the spike samples. Generally, Wellington reported consistently lower recoveries whereas Enviro-Test reported much higher recoveries. Both laboratories had difficulties with spike sample number 1, further suggesting interferences from the matrix at this site (site A).

Table 5

Average Intermediate Level Spike Recoveries

(Per Cent Recoveries)

Sample Number	Wellington	Enviro-Test
7	42	58
10	65	85
33	114	109
52	81	96
Mean	76%	87%
SD	30%	22%
%RSD	40%	25%

At the intermediate spike level, recoveries by both laboratories show more agreement. However, both laboratories had difficulties with spike sample number 7, being also from site A, which is further evidence that there may be something in the matrix from site A causing analytical interference.

Table 6
High Level Spike Recoveries
(Per Cent Recoveries)

Sample Number	Wellington	Enviro-Test
16	119	122
26	71	95
18	64	97
Mean	70%	105%
SD	35%	15%
%RSD	50%	14%

There were significant variations in recovery between laboratories at the high spike level. However, as only three spikes were done at this level, there is insufficient basis to comment further.

In summary the spike recovery data indicates that both laboratories had some difficulties with recovering the known spikes, and that recoveries did not particularly improve as the spike concentrations increased. Still, the spike recoveries were within reasonable ranges as originally set out, thus providing some confidence in the reported analytical data.

iii) Surrogate Recoveries

As part of the extraction procedure, Enviro-Test spiked each sample with an isotope-labelled mixture of tetra to octa dioxins. Surrogate compounds are added to control for possible inefficiencies in sample recovery and subsequent analysis. Surrogate recovery efficiencies are than used to adjust the raw data of the target compounds to provide an actual reported value. The approximate surrogate concentrations were determined to be 182 ppq for the tetra- and penta- dioxins, 364 ppq for the hexa- and hepta- dioxins, and 545 ppq for the octa- dioxin. The laboratory summary of the surrogate data is presented in the Appendix; the overall mean surrogate recovery was 81% with a standard deviation of +/- 25% and a per cent relative standard deviation (%RSD) of 31%. This degree of variation is consistent with that observed for the field spike recoveries.

The spike data, both corrected for and unadjusted by the surrogate recoveries, as well as the surrogate data itself, are generally within the broad range of recovery set out as the minimum acceptable, ie., 70-130% recovery.

iv) Method Detection Limits

The spiking data was used to determine the appropriate method detection limits. The variability in the reported data set with respect to both the field spikes and surrogates demonstrated that the baseline noise or interference was much greater than anticipated. The use of method detection limits (and taking into further account that this work was being done with low resolution mass spectroscopy) was considered very appropriate in determining what level of dioxin/furan in a sample constituted a firm positive value. For this purpose, the United States Environmental Protection Agency has defined "the method detection limit (MDL) as the minimum concentration of a substance that can be measured and reported with 99% confidence that the analyze concentration is greater than zero and is determined from analysis of a sample in a given matrix containing the analyze."

The procedure used for calculating the MDL for each congener group is set out in the Appendix along with the summary of results. The results are reproduced below in Table 7.

b) Field Results

The sampling results from the various community sampling locations are presented in summary form in Table 8.

In summary, Table 8 indicates that dioxins were not found in any of the raw or treated water samples (sampled in duplicate) based on the method detection levels applicable to this study.

At several sites possible trace levels (ie., below the method detection level but above the instrument detection level) of dioxins/furans were found in both the treated waters and the corresponding treated water blanks. One possible explanation might be that airborne dioxins at some sample sites resulted in trace level contamination of all samples collected at that site, including the field blank. This, however, appears unlikely in that for several of the municipalities the physical sampling sites for obtaining the raw and treated water sets were the same. Therefore, both raw and treated water sample sets should have experienced the same contamination; but this was not the case as the raw samples did not exhibit any contamination.

Table 7

Calculated Method Detection Limits (MDL)
and Instrument Detection Limits
(in ppq)

	Enviro-Test		Wellington	
	Instrument Limit	MDL	Instrument Limit	MDL
T4CDD	5	18.3	5	13.2
P5CDD	5	22.2	5	12.3
H6CDD	5	20.0	5	24.6
H7CDD	10	23.1	10	47.2
O8CDD	10	67/4	10	70.1
T4CDF	5	11.0	1	6.6
P5CDF	5	16.3	2	13.3
H6CDF	5	36.9	2	29.0
H7CDF	10	45.1	3	39.9
O8CDF	10	45.1	5	61.1

Table 8
Summary of Dioxin Sampling Results

Location	Sample Type	Field Blank	Field Spike (% Rec'y)	Duplicate Samples A	B
A	Raw	nd	42%	nd	nd
	Treated	nd	45%	nd	nd
B	Raw	nd-xh	119%	nd-x	nd-xh
	Treated	nd-x	65%	nd	nd-x
C	Raw	nd	66%	nd-x	nd-x
	Treated	nd-x	64%	nd-x	nd-xh
D	Raw	nd	114%	nd	nd
	Treated	nd	71%	nd	nd
	Inter.	nd	109%	nd	nd
E	Raw	nd-x	88%	nd	nd-x
F	Raw	nd	72%	nd	nd
	Treated	nd-x	81%	nd-x	nd-x
G	Raw	nd	100%	nd	nd
	Treated	nd-x	93%	nd-x	nd-x

Notes: nd -- not detectable; based on both the lower instrument detection limits and the higher method detection limits ie., below 1-5 ppq depending upon congener group.

nd-x -- not detectable; below the methods detection limit but some congener groups identified at slightly above the instrument detection level, ie., 1-12 ppq range. The implication is that statistically the reported value can not be distinguished sufficiently from zero (not detected).

nd-xh -- not detectable; near the upper level of the methods detection range for some congener groups, ie., 6-70 ppq range, but with results questionable from a QA/QC perspective. (These particular samples are suspect due to possible laboratory contamination during processing. These samples all display approximately the same distribution of furans, in the same concentrations, and were all processed at the same time in one batch.)

Another possibility considered and investigated was that sample contamination could have been associated with the addition of the various ampoules to each bottle as part of the overall blind spiking protocol. A number of ampoules were selected at random and processed as controls with no detection of dioxins.

The possibility that the source of contamination originated within the laboratory was also considered. As noted previously there was one batch of samples processed together which showed a common level and distribution of furan contamination. Further review of the laboratory sequence for both extraction and cleanup indicated a possible correlation between trace level contamination within a given sample set and batching of samples for the cleanup procedure. However, further direct investigation of this possibility could not be pursued since all processing had been completed by that time.

Therefore, there is no clear explanation as to the source of the trace contamination in the treated water and treated water blanks. Still, the fact that the trace contamination was detected in the field blanks indicates the corresponding treated water sample results are suspect and that dioxins/furans are not likely present in the treated waters at these community locations.

5) Discussion and Conclusions

The overall objective of this sampling program was to determine whether dioxins were present in drinking waters downstream from bleached kraft mill effluent discharges. Such information was considered necessary to address the issues of dioxin exposure via drinking water and associated public health considerations while developing a database which would be useful for comparison purposes should further pulp mill development occur in these watersheds.

Dioxins were not detected in either the raw or treated waters at any of the municipal sites sampled within the limits of the method detection levels demonstrated for this study. The methods detection level was in the range 6-70 ppq depending upon congener group. As such, there does not appear to be a quantitated exposure to dioxins via drinking water at the sampling sites investigated, and consequently no undue impact on water quality and associated human health. All valid samples were below the Ontario tentative standard of 15 ppq on an equivalency basis.

It was anticipated that detection levels in the 1-5 ppq range would be achieved in this study. Several measures were taken in an attempt to achieve the desired level of detection including: large volume sampling; the collection of multiple samples; and a validation study of the methodology. A number of additional quality control measures were also followed within the laboratories. However, the results from this study indicate that such low detection levels (1 to 5 ppq) are not as yet readily achievable and that practical detection levels for dioxins are considerably higher, especially for the higher congener groups.

Varying values of dioxins were reported based on instrument detection limits. The quality control information from this study dictates that such data must be viewed with caution. Two areas among many where variability can arise are: matrix interferences and low level laboratory contamination. It is considered that both of these problems were encountered in this study. It is for these and other reasons that the method detection limit concept was adopted in identifying non-zero values for valid samples.

Both laboratories experienced the same types of recovery and contamination problems which confirms that the difficulties lie with the initial processing of samples. Both laboratories had difficulties in recoveries from the same sites, indicating the matrix to be a major confounding factor. Similarly, both laboratories confirmed the low level contamination of blanks and regular samples thereby indicating the problem did not reside with the analysis step but at some point earlier in sample collection or processing.

In view of the difficulties highlighted within this study, a rigorous QA/QC program is considered mandatory and without such a program interpretation of data is not desireable nor prudent. It is also essential that other criteria for acceptance of positive results be in place in addition to instrument and method performance.

Leaving aside the issue of QA/QC, it was interesting to note that of the trace contaminants found, most were various furans. None of the tetra- dioxin congener group was observed. The only dioxin congener observed was the octa- dioxin. Therefore, there does not appear to be a problem of dioxins in the raw or treated drinking waters downstream from existing bleached kraft mill discharges. Even though the method detection range proved to be higher than originally desired, the sampling program did establish an upper limit on possible dioxins/furans, and this upper limit is reflected in the method detection levels for the specific congener group.

References

1. DIOXINS - DISASTER OR DIVERSION? John Leach, British Columbia Research Corporation, Vancouver, British Columbia. Paper presented at the CPPA Environmental Conference, Vancouver, October 25-27, 1988.

2. Clement, R. E., and Tosine, H. M., Mass Spectrometry Review 1988, 7, 593-636.

3. DIOXINS AND FURANS: THE CANADIAN PERSPECTIVE Canadian Council of Resource and Environmental Ministers (no date)

Appendix A

NORMALIZED DATA

SUMMARY OF ANALYTICAL DATA ON A MUNICIPAL BASIS

NOTES TO TABLES FOLLOWING:

1. For sake of brevity, dioxin and furan congener groups have been abbreviated and listed simply as a number/letter combination, i.e., 8D (octa dioxins) or 5F (penta furans), followed by the analytical concentration in ppq rounded to the nearest whole number.
2. In a number of cases, two values are reported for a particular congener group. This would occur when both laboratories reported results for a particular sample.
3. The summarized data reflects claimed instrument detection levels rather than method detection levels. This has been done to give the reader a sense of the magnitude of the raw data, without taking into consideration quality assurance and control aspects.
4. Field spiking levels are reported in the tables as (1x), (2x) or (3x) under the Field Spike heading.

TABLE A.1

SAMPLE CODE: E
BASIN: ATHABASCA RIVER
MUNICIPAL LOCATION: JASPER
SAMPLE SITE: ATHABASCA RIVER AT JASPER

SAMPLE TYPE	FIELD BLANK	FIELD SPIKE (1X)	REGULAR SAMPLE	DUPLICATE SAMPLE
SAMPLE NUMBER:	39	30	29	40
RESULT:	6F -3 ppq 8F -6 ppq	R: 88% 127%	N.D.	6F -3 ppq 7F -4 ppq

TABLE A.2

SAMPLE CODE: D
BASIN: ATHABASCA RIVER
MUNICIPAL LOCATION: HINTON
SAMPLE SITE: RAW AT PUMPHOUSE; RAW AT PLANT; TREATED

SAMPLE TYPE	FIELD BLANK	FIELD SPIKE	REGULAR SAMPLE	DUPLICATE SAMPLE
RAW WATER AT PUMPHOUSE		(2X)		
SAMPLE NUMBER:	35	33	31	37
RESULT:	N.D.	R: 114% 109%	N.D.	N.D.
RAW WATER AT PLANT		(1X)		
SAMPLE NUMBER:	36	34	32	38
RESULT:	N.D.	R: 128% 109%	N.D.	N.D.
TREATED WATER		(3X)		
SAMPLE NUMBER:	27	26	25	28
RESULT:	N.D.	R: 71% 95%	N.D.	N.D.

TABLE A.3

SAMPLE CODE: B

BASIN: ATHABASCA RIVER

MUNICIPAL LOCATION: SMITH

SAMPLE SITE: RAW AND TREATED WATER AT WATER TREATMENT PLANT

SAMPLE TYPE	FIELD BLANK	FIELD SPIKE	REGULAR SAMPLE	DUPLICATE SAMPLE
RAW WATER		(3X)		
SAMPLE NUMBER:	14	16	13	15
RESULT:	8D -18,13 ppq	R: 119%	8D -10	8D -11 ppq
	4F -42,20	127%	4F -13,8	4F -32,23
	5F -65,44		5F -9,7	5F -54,35
	6F -70,36		6F -9,8	6F -60,34
	7F -49,21		7F -6	7F -39,20
	8F -51,44		8F -9	8F -45,38
TREATED WATER:		(2X)		
SAMPLE NUMBER:	12	10	9	11
RESULT:	8D -12 ppq	R: 65%	N.D.	8D -12 ppq
	4F -10	85%		4F -5,6
	5F -7,8			5F -6,7
	6F -5,5			8F -6

TABLE A.4

SAMPLE CODE: A

BASIN: ATHABASCA RIVER

MUNICIPAL LOCATION: ATHABASCA

SAMPLE SITE: RAW AND TREATED WATER AT WATER TREATMENT PLANT

SAMPLE TYPE	FIELD BLANK	FIELD SPIKE	REGULAR SAMPLE	DUPLICATE SAMPLE
RAW WATER		(2X)		
SAMPLE NUMBER:	8	7	6	5
RESULT:	N.D.	R: 42% 58%	N.D.	N.D.
TREATED WATER		(1X)		
SAMPLE NUMBER:	2	1	4	3
RESULT:	N.D.	R: 45% 71%	N.D.	N.D.

TABLE A.5

SAMPLE CODE: F

BASIN: PEACE RIVER

MUNICIPAL LOCATION: GRANDE PRAIRIE

SAMPLE SITE: RAW AND TREATED WATER AT WATER TREATMENT PLANT

SAMPLE TYPE	FIELD BLANK	FIELD SPIKE	REGULAR SAMPLE	DUPLICATE SAMPLE
RAW WATER		(1X)		
SAMPLE NUMBER:	59	60	58	57
RESULT:	N.D.	R: 72% 100%	N.D.	N.D.
TREATED WATER:		(2X)		
SAMPLE NUMBER:	49	52	51	50
RESULT:	4F -2 ppq 5F -2 6F -6 7F -4	R: 81% 96%	4F -2 ppq 6F -4 ppq 6f -6	

TABLE A.6

SAMPLE CODE: G

BASIN: PEACE RIVER

MUNICIPAL LOCATION: PEACE RIVER

SAMPLE SITE: RAW AND TREATED WATER AT WATER TREATMENT PLANT

SAMPLE TYPE	FIELD BLANK	FIELD SPIKE	REGULAR SAMPLE	DUPLICATE SAMPLE
RAW WATER		(1X)		
SAMPLE NUMBER:	56	55	54	53
RESULT:	N.D.	R: 100% 159%	N.D.	N.D.
TREATED WATER:		(1X)		
SAMPLE NUMBER:	46	45	47	48
RESULT:	4F -1 ppq 5F -4 6F -4 7F -3	R: 93% 117%	4F -1 ppq 5F -5 6F -7 7F -5	4F -1 ppq 6F -3

TABLE A.7

SAMPLE CODE: C

BASIN: PEACE RIVER

MUNICIPAL LOCATION: FORT VERMILLION

SAMPLE SITE: RAW AND TREATED WATER AT WATER TREATMENT PLANT

SAMPLE TYPE	FIELD BLANK	FIELD SPIKE	REGULAR SAMPLE	DUPLICATE SAMPLE
RAW WATER		(3X)		
SAMPLE NUMBER:	23	22	21	24
RESULT:	N.D.	R: 66%	4F -6 ppq	4F -5 ppq
		127%	5F -7	5F -4
			6F -12,5	6F -11
			7F -5	8F -8,11
			8F -8	
TREATED WATER:		(3X)		
SAMPLE NUMBER:	19	18	20	17
RESULT:	4F -4 ppq	R: 64%	4F -3 ppq	4F -23,19
	5F -3	97%	5F -5	5F -65,33
	6F -5		6F -7,7	6F -35,29
	8F -7		8F -6	7F -24,18
				8F -14,31

APPENDIX B

RAW DATA

Raw data is included in three separate reports received from the two contracted laboratories. The raw data is only included with the original of this report; copies may be viewed on request or copies made if actually required.